Effect of counterions on properties of micelles formed by alkylpyridinium surfactants .1. Conductometry and H-1-NMR chemical shifts

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Effect of Counterions on Properties of Micelles Formed by Alkylpyridinium Surfactants. 1. Conductometry and ^{1}H-NMR Chemical Shifts

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This paper delineates the influence of counterions on the aggregation behavior of 1-methyl-4-*n*-dodecylpyridinium surfactants, using conductometry and ^{1}H-NMR spectroscopy. Three types of counterions have been studied: (i) halides, (ii) alkanesulfonates, and (iii) aromatic counterions. The critical micelle concentration is found to decrease with increasing counterion size and increasing counterion hydrophobicity, whereas the degree of counterion binding increases. The aggregation behavior of 1-methyl-4-*n*-dodecylpyridinium surfactants with aromatic counterions is shown to be markedly dependent on the substituent (hydrophobicity) and the substitution pattern in the aromatic ring of the counterion. Depending on the molecular architecture of the aromatic counterion, extremely long wormlike micelles can be formed instead of (nearly) spherical micelles. NMR experiments revealed that all aromatic counterions intercalate in between the pyridinium headgroups of the micelles, with more or less the same degree of penetration. All results can be explained on the basis of counterion−surfactant and counterion−water interactions, taking into account the specific microenvironment in the Stern layer.

Introduction

Aggregation of surfactant monomers in water can lead to the formation of a variety of aggregate morphologies including micelles, vesicles, and inverted structures. At low concentrations (i.e. below the cmc, the critical micelle concentration) ionic surfactants behave like simple electrolytes. Above the critical micelle concentration (cmc, for spherical micelles, and cwmc for wormlike micelles), the monomers assemble to form aggregates.[1] The cmc is by far the most extensively studied micellar property and is related to the thermodynamic stability of the micelles. Critical micelle concentrations can be measured by a wide variety of techniques.[2−5] The critical micelle concentrations slightly depend on the method used. Apart from the molecular architecture of a surfactant, critical micelle concentrations depend[6] on temperature, pressure, and added electrolyte (ionic strength). The chain length and chain branching of the hydrophobic moiety of a surfactant are two important structural parameters which determine the cmc. Usually,[7] the cmc decreases upon increasing chain length of the hydrophobic moiety and increases upon increasing degree of branching. In the case of ionic surfactants, micellization is hampered by electrostatic headgroup repulsions. Counterions influence this process by altering headgroup interactions.

This paper examines the role of counterions in determining the properties of micelles formed by 1-methyl-4-*n*-dodecylpyridinium surfactants (**1**−**17**). These properties include the cmc, the degree of counterion binding, and the degree of penetration of aromatic counterions between the headgroups.

With respect to the surfactant the following structural features will be discussed (see Chart 1): (i) the size of the counterion (**1**−**3**), (ii) the counterion hydrophobicity (**4**−**8**), and (iii) the effect of aromatic counterions (**9**−**17**). The cmc values were determined using electrical conductivities. From the ratio of the slopes of plots of conductivity versus concentration below and above the cmc the degree of counterion binding (β) was calculated. Absolute values may not be fully reliable,[8] but trends within a series of structurally related surfactants can be compared with confidence, particularly since only the counterion is varied. NMR measurements on surfactants with aromatic counterions provided information on the positions of counterions in micelles.

Experimental Section

General Methods. The water used in all experiments was demineralized and distilled twice in an all-quartz distillation unit. All commercially available chemicals were purchased from Merck, Aldrich, Janssen, or Fluka and were used without further purification.

Elemental analyses were performed in the microanalytical department of our laboratories by Mr. H. Draayer, Mr. J. Ebels, and Mr. J. Hommes.

NMR Measurements. ^{1}H NMR spectra were recorded using a Varian VXR-300 (300 MHz) instrument or on a Nicolet NT-200 spectrometer (200 MHz). All spectra were recorded in either $CDCl_3$ or D_2O, as indicated for each spectrum. The ^{1}H chemical shifts are reported in δ units (ppm) relative to the solvent as an internal standard and are converted to the TMS scale. TMS (tetramethylsilane) as a standard absorps at $\delta = 0.00$ ppm, using $\delta(CHCl_3) = 7.24$ ppm and $\delta(DOH) = 4.65$ ppm. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); b (broad); m (multiplet). ^{13}C NMR spectra were recorded on a Nicolet NT-200 spectrometer. The chemical shifts are denoted in δ units (ppm) with the solvent as an internal standard and are converted to the TMS scale using $\delta(CDCl_3) = 76.9$ ppm. ^{19}F NMR spectra were recorded on a Nicolet NT-200 spectrometer. The chemical shifts are denoted in δ units (ppm) with the solvent as an internal standard and are converted to the TMS scale using $\delta(CCl_3F) = 0$ ppm.

Synthetic Procedures. The synthesis of surfactants **1**,[9] **2**,[10] and **3**[9] has been described previously. The novel surfactants

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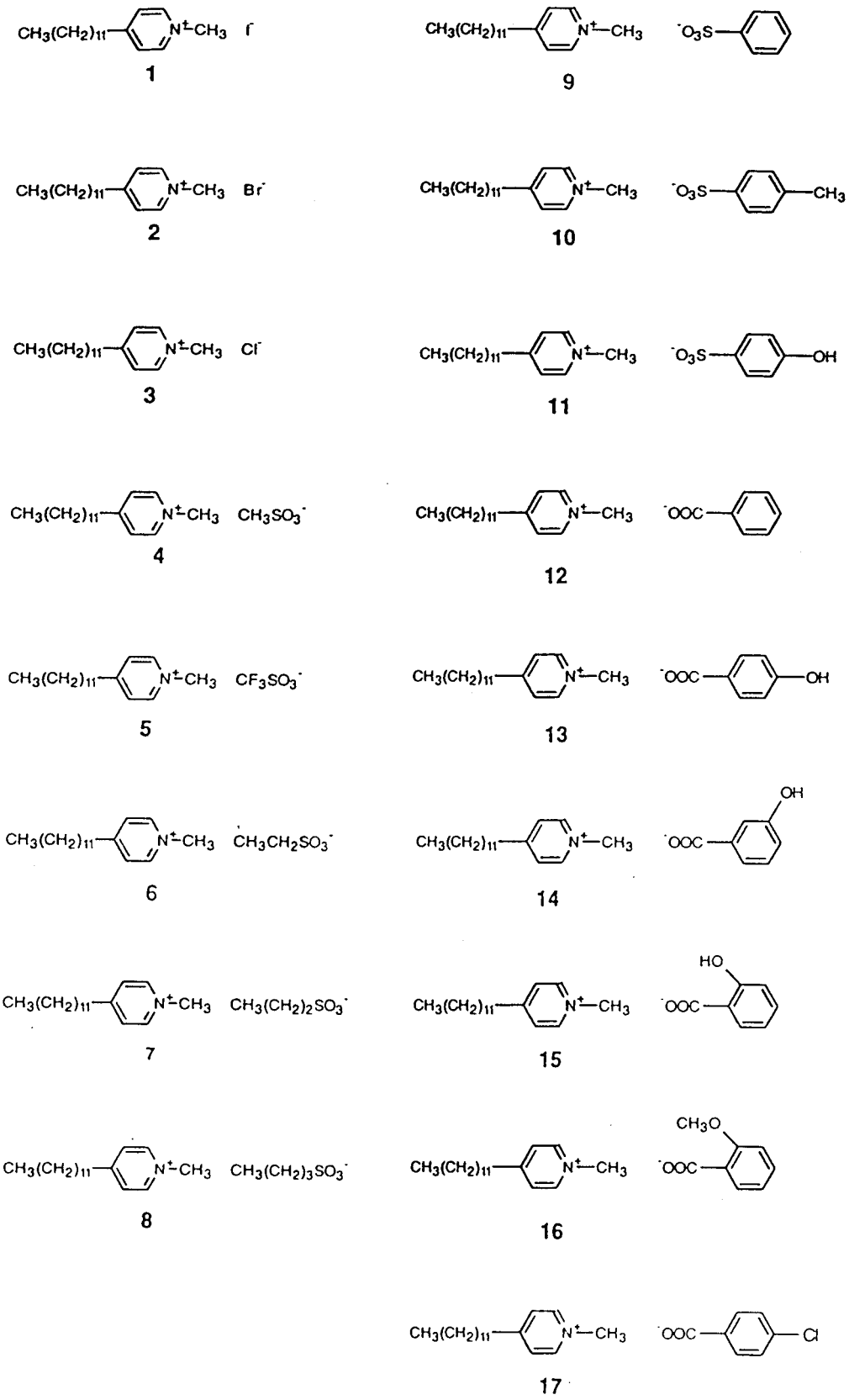
Chart 1



(**4**−**17**, Chart 1) were prepared using ion-exchange methods. An ion-exchange column was made with Dowex 1 × 8 200−400 mesh (Merck). After regeneration with the sodium salt of the desired anionic counterion, the column was washed with water (2 L) and methanol (0.5 L). Compound **1** was dissolved in 3 mL of methanol and introduced on the column. The product was fractionally collected in 20 mL tubes. The tubes which contained product (using a UV detection test) were combined, and the solvent was subsequently evaporated using a rotatory evaporator. The product was crystallized from THF−ether mixtures. Finally the compound was freeze-dried overnight. For surfactants **12**−**17** it was not possible to remove all water, because the surfactants are strongly hygroscopic (best results were obtained after freeze drying; no impurities were detected using NMR).

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1-Methyl-4-*n*-dodecylpyridinium Methanesulfonate (4). ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 0.82$ (3H, t), 1.21 (18H, b), 1.64 (2H, t), 2,69 (3H, s), 2.80 (2H, t), 4.57 (3H, s), 7.75 (2H, d), 9.26 (2H, d) ppm. ^{13}C-NMR ($CDCl_3$, 300 MHz): $\delta = 13.4$ (CH_3, alkyl chain), 22.0−35.2 (CH_2, alkyl chain), 47.3 (N^+-CH_3), 63.8 (CH_3, counterion), 127.0 (CH, pyridinium ring), 144.8 (CH, pyridinium ring), 162.0 (C, pyridinium ring) ppm.

Anal. Calcd: C, 63.83; H, 9.86; N, 3.92; S, 8.96. Found: C, 63.61; H, 9.86; N, 3.95; S, 8.68.

1-Methyl-4-*n*-dodecylpyridinium Trifluoromethanesulfonate (5). ^{1}H-NMR (DMSO, 200 MHz): $\delta = 0.84$ (3H, t), 1.23 (18H, b), 1.63 (2H, t), 2.84 (2H, t), 4.27 (3H, s), 7.97 (2H, d), 8.84 (2H, d) ppm. ^{13}C-NMR (DMSO, 200 MHz): $\delta = 13.9$ (CH_3, alkyl chain), 22.1−34.5 (CH_2, alkyl chain), 47.1 (N^+-CH_3), 51.3 (CF_3, counterion), 127.2 (CH, pyridinium ring), 144.8 (CH, pyridinium ring), 162.0 (C, pyridinium ring) ppm. ^{19}F-NMR: $\delta = -76.5$ (CF_3, counterion) ppm.

1-Methyl-4-*n*-dodecylpyridinium Ethanesulfonate (6). ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.79$ (3H, t), 1.18 (21H, b), 1.62 (2H, t), 2,77 (4H, m), 4.52 (3H, s), 7.73 (2H, d), 9.28 (2H, d) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): $\delta = 9.9$ (CH_3, counterion), 14.0 (CH_3, alkyl chain), 22.6−35.7 (CH_2, alkyl chain), 45.8 (CH_2, counterion) 47.7 (N^+-CH_3), 127.6 (CH, pyridinium ring), 145.5 (CH, pyridinium ring), 162.5 (C, pyridinium ring) ppm.

1-Methyl-4-*n*-dodecylpyridinium *n*-Propanesulfonate (7). ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.82$ (3H, t), 0.94 (3H, t), 1.20 (18H, b), 1.60 (4H, m), 2.78 (4H, m), 4.52 (3H, s), 7.74 (2H, d), 9.22 (2H, d) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): $\delta = 13.5$ (CH_3, counterion), 14.0 (CH_3, alkyl chain), 18.9−35.7 (CH_2, alkyl chain and counterion), 47.8 (N^+-CH_3), 54.0 (CH_2, counterion), 127.6 (CH, pyridinium ring), 145.5 (CH, pyridinium ring), 162.5 (C, pyridinium ring) ppm.

Anal. Calcd: C, 65.41; H, 10.19; N, 3.63; S, 8.31. Found: C, 66.22; H, 10.15; N, 3.77; S, 6.95.

1-Methyl-4-*n*-dodecylpyridinium *n*-Butanesulfonate (8). ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.90$ (6H, b), 1.24 (20H, b), 1.52 (4H, b), 2.80 (4H, b), 4.53 (3H, b), 7.74 (2H, b), 9.13 (2H, b) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): $\delta = 13.7$ (CH_3, counterion), 14.1 (CH_3, alkyl chain), 21.9−35.6 (CH_2, alkyl chain and counterion), 47.8 (N^+-CH_3), 51.3 (CH_2, counterion), 127.8 (CH, pyridinium ring), 144.9 (CH, pyridinium ring), 162.7 (C, pyridinium ring) ppm.

Anal. Calcd: C, 66.12; H, 10.34; N, 3.50; S, 8.02. Found: C, 66.63; H, 10.22; N, 3.54; S, 6.88.

1-Methyl-4-*n*-dodecylpyridinium Benzenesulfonate (9). ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.88$ (3H, t), 1.26 (18H, b), 1.61 (2H, t), 2.76 (2H, t), 4.50 (3H, s), 7.33 (3H, m), 7.63 (2H, d), 7.85 (2H, m), 9.03 (2H, d) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): $\delta = 14.1$ (CH_3, alkyl chain), 22.6−35.7 (CH_2, alkyl chain), 47.9 (N^+-CH_3), 125.9 (CH, counterion), 127.6 (CH, pyridinium ring), 128.1 (CH, counterion), 129.3 (CH, counterion), 145.2 (CH, pyridinium ring), 146.2 (C, counterion), 162.5 (C, pyridinium ring) ppm.

Anal. Calcd: C, 68.69; H, 8.89; N, 3.34; S, 7.64. Found: C, 68.85; H, 8.84; N, 3.27; S, 7.30.

1-Methyl-4-*n*-dodecylpyridinium Tosylate (10). ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.79$ (3H, t), 1.17 (18H, b), 1.50 (2H, t), 2.23 (3H, s), 2.64 (2H, t), 4.30 (3H, s), 7.02 (2H, d), 7.52 (2H, d), 7.63 (2H, d), 8.95 (2H, d) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): $\delta = 14.0$ (CH_3, alkyl chain), 21.2 (CH_3, counterion), 22.6−35.6 (CH_2, alkyl chain), 47.6 (N^+-CH_3), 125.7 (CH, counterion), 127.5 (CH, pyridinium ring), 128.6 (CH, counterion), 139.2 (C, counterion), 144.1 (C, counterion), 145.3 (CH, pyridinium ring), 162.2 (C, pyridinium ring) ppm.

Anal. Calcd: C, 68.37; H, 9.32; N, 3.22; S, 7.60. Found: C, 68.47; H, 8.91; N, 3.12; S, 7.24.

1-Methyl-4-*n*-dodecylpyridinium 4-Hydroxybenzenesulfonate (11). ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.84$ (3H, t), 1.22 (18H, b), 1.52 (2H, t), 2.65 (2H, t), 4.09 (3H, s), 6.69 (2H, d), 7.47 (4H, m), 8.53 (2H, d) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): $\delta = 14.1$ (CH_3, alkyl chain), 22.6−35.6 (CH_2, alkyl chain), 47.4 (N^+-CH_3), 115.0 (CH, counterion), 127.3−127.5 (CH, pyridinium ring and counterion), 136.9 (C, counterion), 144.5 (CH, pyridinium ring), 158.8 (C, counterion), 162.5 (C, pyridinium ring) ppm.

Anal. Calcd: C, 66.17; H, 8.56; N, 3.22; S, 7.36. Found: C, 65.87; H, 8.46; N, 3.27; S, 7.39.

1-Methyl-4-*n*-dodecylpyridinium Benzoate (12). ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.84$ (3H, t), 1.21 (18H, b), 1.44 (2H, t), 2.55 (2H, t), 4.46 (3H, s), 7.21 (3H, m), 7.47 (2H, d), 7.91 (2H, m), 9.10 (2H, d) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): $\delta = 14.1$ (CH_3, alkyl chain), 22.6−35.5 (CH_2, alkyl chain), 47.3 (N^+-CH_3), 127.4 (CH, pyridinium ring), 129.2 (CH, counterion), 139.5 (C, counterion), 145.3 (CH, pyridinium ring), 161.9 (C, pyridinium ring), 172.0 (COO^-, counterion) ppm.

Anal. Calcd: C, 77.58; H, 10.04; N, 3.77. Found: 78.19; H, 9.86; N, 3.63.

1-Methyl-4-*n*-dodecylpyridinium 4-Hydroxybenzoate (13). ^{1}H-NMR (DMSO, 200 MHz): $\delta = 0.83$ (3H, t), 1.22 (18H, b), 1.60 (2H, t), 2.80 (2H, t), 4.27 (3H, s), 6.71 (2H, d), 7.67 (2H, d), 7.93 (2H, d), 8.90 (2H, d) ppm. ^{13}C-NMR (DMSO, 200 MHz): $\delta = 13.9$ (CH_3, alkyl chain), 22.1−34.5 (CH_2, alkyl chain), 47.0 (N^+-CH_3), 114.1 (CH, counterion), 127.2 (CH, pyridinium ring), 128.6 (C, counterion), 130.6 (CH, counterion), 144.8 (CH, pyridinium ring), 160.0 (COH, counterion), 161.9 (C, pyridinium ring), 169.3 (COO^-, counterion) ppm.

Anal. Calcd (0.5% crystal water): C, 73.49; H, 9.37; N, 3.43. Found: C, 73.06; H, 9.08; N, 3.46.

1-Methyl-4-*n*-dodecylpyridinium 3-Hydroxybenzoate (14). ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.85$ (3H, t), 1.23 (18H, b), 1.39 (2H, t), 2.49 (2H, t), 4.28 (3H, s), 6.63 (1H, d), 6.89 (1H, t), 7.30 (3H, m), 7.39 (1H, s), 8.78 (2H, d) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): $\delta = 14.1$ (CH_3, alkyl chain), 22.6−35.4 (CH_2, alkyl chain), 47.4 (N^+-CH_3), 116.3 (CH, counterion), 117.4 (CH, counterion), 119.6 (CH, counterion), 127.1 (CH, pyridinium ring), 128.5 (CH, counterion) 139.7 (C, counterion), 144.7 (CH, pyridinium ring), 157.8 (COH, counterion), 161.8 (C, pyridinium ring), 172.1 (COO^-, counterion) ppm. Anal. Calc (0.5% crystal water): C, 73.49; H, 9.37; N, 3.43. Found: 73.38; H, 9.45; N, 3.41.

1-Methyl-4-*n*-dodecylpyridinium 2-Hydroxybenzoate (15). ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.85$ (3H, t), 1.22 (18H, b), 1.50 (2H, t), 2.63 (2H, t), 4.37 (3H, s), 6.65 (2H, m), 7.10 (1H, m), 7.49 (2H, d), 7.73 (1H, m), 8.79 (2H, d) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): $\delta = 14.1$ (CH_3, alkyl chain), 22.6−35.6 (CH_2, alkyl chain), 47.7 (N^+-CH_3), 116.1 (CH, counterion), 117.1 (CH, counterion), 119.9 (C, counterion), 127.4 (CH, pyridinium ring), 130.3 (CH, counterion), 132.1 (CH, counterion), 144.6 (CH, pyridinium ring), 162.1 (C, pyridinium ring), 162.7 (COH, counterion), 173.6 (COO^-, counterion) ppm.

Anal. Calc (0.5% crystal water): C, 73.49; H, 9.37; N, 3.43. Found: C, 73.50; H, 9.37; N, 3.34.

1-Methyl-4-*n*-dodecylpyridinium 2-Methoxybenzoate (16). ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.83$ (3H, t), 1.21 (18H, b), 1.54 (2H, t), 2.66 (2H, t), 3.67 (3H, s), 4.43 (3H, s), 6.74 (2H, m), 7.08 (1H, m), 7.39 (1H, m), 7.50 (2H, d), 9.42 (2H, d) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): $\delta = 14.0$ (CH_3, alkyl chain), 22.2−35.8 (CH_2, alkyl chain), 47.5 (N^+-CH_3), 55.8 (OCH_3, counterion), 111.0 (CH, counterion), 120.0 (CH, counterion), 127.1 (CH, pyridinium ring), 128.0 (CH, counterion), 128.3 (CH, counterion), 133.2 (C, counterion), 146.0 (CH, pyridinium ring), 155.8 (CO, counterion), 161.9 (C, pyridinium ring), 172.1 (COO^-, counterion) ppm.

Anal. Calc (0.5% crystal water): C, 73.89; H, 9.54; N, 3.31. Found: C, 73.83; H, 9.38; N, 3.36.

1-Methyl-4-*n*-dodecylpyridinium 4-Chlorobenzoate (17). ^{1}H-NMR (DMSO, 200 MHz): $\delta = 0.83$ (3H, t), 1.22 (18H, b), 1.61 (2H, t), 2.83 (2H, t), 4.32 (3H, s), 7.23 (2H, d), 7.80 (2H, d), 7.97 (2H, d), 8.99 (2H, d) ppm. ^{13}C-NMR (DMSO, 200 MHz): $\delta = 13.9$ (CH_3, alkyl chain), 22.1−34.5 (CH_2, alkyl chain), 47.0 (N^+-CH_3), 126.7 (CH, counterion), 127.2 (CH, pyridinium ring), 130.7 (CH, counterion), 132.2 (C, counterion), 140.8 (C, counterion), 145.0 (CH, pyridinium ring), 161.8 (C, pyridinium ring), 167.5 (COO^-, counterion) ppm.

Anal. Calc (0.5% crystal water): C, 70.32; H, 8.73; N, 3.28; Cl, 8.30. Found: C, 70.28; H, 8.56; N, 3.24; Cl, 8.36.

Cmc Measurements. Critical micelle concentrations and degrees of counterion binding were determined using conductivity measurements. Conductivities were measured using a Wayne-Kerr Autobalance Universal Bridge B642 fitted with a Philips electrode PW 9512101 with a cell constant of 0.71 cm^{-1}. The solutions were thermostated in the cell for at least 15 min before measurements were initiated. The conductivity cell was equipped with a magnetic stirring device. The surfactant concentration in the cell was increased by addition (microsyringe) of 30−50 μL aliquots of a concentrated surfactant solution to the conductivity

Table 1. Critical Micelle Concentration (cmc), Degree of Counterion Binding (β), and Volumes of the Hydrated Ions (V_{ih}^{∞}(compress.)) for 1-Methyl-4-*n*-dodecylpyridinium Halide Surfactants at 30 °C

surfactant	cmc (mM)	β (%)	V_{ih}^{∞}(compress.)[b] ($cm^3\ mol^{-1}$)
1	2.50[a]	82[a]	37.1
2	4.95[a]	71[a]	61.9
3	5.5	63	72.9

[a] According to ref 10. [b] According to ref 12.

medium. Concentrations were corrected for volume changes. Cmc values were taken from the intersection of the tangents drawn before and after the break in the conductivity vs concentration plot. The degree of counterion binding is taken as 1 minus the ratio of slopes of the conductivity versus concentration curve above and below of the cmc.

Krafft Temperature. Krafft temperatures were determined by monitoring the turbidity on slowly increasing the temperature using a Philips PU 8740 UV/vis spectrophotometer equipped with a Haake F3 water bath. In a typical experiment 50 mg of surfactant was heated in 2 mL of demineralized water.

Results and Discussion

Influence of Counterion Size on the Aggregation of 1-Methyl-4-*n*-dodecylpyridinium Halide Surfactants in Aqueous Solution. For ionic surfactants, micellization is hampered by electrostatic repulsions between charged headgroups. Below the cmc the surfactant cation and counteranion are fully dissociated. When micelles are formed, counterions are adsorbed at the micellar surface, thus reducing the charge density and facilitating micellization. Counterions are bound primarily by the strong electrostatic field at the micellar surface created by headgroups which are in close proximity, and sometimes also by specific interactions that depend on the nature of the headgroups and counterions. The degree of counterion adsorption at micellar surfaces depends, for halide surfactants, on the hydration Gibbs energy of the counterions. It has been suggested[11] that the degree of counterion binding is inversely proportional to the effective radius of the hydrated ion. In the absence of specific counterion effects, the degree of surface stabilization is determined by electrostatics.

The influence of the size of the counterion on the aggregation behavior of 1-methyl-4-*n*-dodecylpyridinium halide surfactants is summarized in Table 1. As the counterion is varied from iodide to bromide to chloride, the cmc, which is a measure of the thermodynamic stability of the micelle, increases and the degree of counterion binding decreases. As a consequence of the increase in size of the hydrated ion,[12] hydrated chloride counterions are located further away from the micellar surface than hydrated iodide counterions. The resulting increase in effective charge at the micellar surface increases the cmc and the Gibbs energy of micellization. Consistently, for *n*-dodecyltrimethylammonium salts the cmc follows the sequence[13] $NO_3^- < Br^- < Cl^-$.

For a structurally related series of cationic surfactants, e.g. *n*-dodecylpyridinium micelles, the binding of counterions to micelles also decreases with increasing hydration,[14] e.g. $I^- > Br^- > Cl^- > CH_3COO^-$. Apart from the cmc and degree of counterion binding, other micellar properties also depend on the counterion size and follow a Hofmeister or lyotropic series. The aggregation number (N), for example, increases with decreasing size of the hydrated counterion.[15]

Influence of Counterion Hydrophobicity on the Properties of Micelles Formed by 1-Methyl-4-*n*-dodecylpyridinium Surfactants. In the following discussion we focus on organic counterions which can penetrate between the headgroups of surfactants. Apart from electrostatic interactions, additional counterion effects (e.g. London dispersion interactions between counterion and surfactant monomer) play a significant role. A prerequisite for the penetration of organic counterions in between headgroups of surfactant monomers in a micelle is that the counterions contain a hydrophobic moiety. This hydrophobic moiety may have favorable interactions with the headgroups but also with the methylene groups of the hydrophobic chain in the surfactant, thereby facilitating micellization. Previously it was found that counterion hydrophobicity has a large influence on the micellization of *n*-decylammonium surfactants.[16] Aggregation numbers increase upon increasing counterion hydrophobicity.[16]

Sepúlveda et al.[17] studied the properties of micelles formed by cetyltrimethylammonium surfactants as a function of counterion hydrophobicity. On going from benzenesulfonate to tosylate to *p*-ethylbenzenesulfonate to *p*-*n*-propylbenzenesulfonate, cmc values decrease, and degrees of counterion binding increase, indicating stronger interactions between the counterions and the micellar surface. The same authors found an increase in relative viscosity upon increasing counterion hydrophobicity, consistent with the presence of larger aggregates. Using light-scattering techniques, Underwood and Anacker[18] determined critical micelle concentrations and aggregation numbers for *n*-decyltrimethylammonium micelles with ethanoate, propionate, isobutyrate, pivalate, phenylacetate, and diphenylacetate as counterions. The counterion effectiveness in reducing the cmc and the increase of the aggregation number were interpreted in terms of hydrophobic interactions. Underwood and Anacker[18] also concluded that the micellar surface is a fluid region which can easily accommodate a variety of insertions.

The data for our surfactants show that an increase in counterion hydrophobicity (i.e. the R moiety of the RSO_3^- counterion), expressed as the sum of Rekker's[19] hydrophobic fragmental constants ($\sum f_i$), lowers the cmc and increases the degree of counterion binding (Table 2).

The cmc and degree of counterion binding for surfactant **8** are rather unexpected. On the basis of hydrophobicity, a lower cmc and higher degree of counterion binding were anticipated. More hydrophobic counterions not only lead to an increase in aggregation number but eventually (as, for example, in the case of SDS/CTAB mixtures) may induce the formation of vesicles. However, no vesicles were detected for surfactant **8**, using transmission electron microscopy. Moroi et al.[21] studied the aggregation of *n*-dodecyltrimethylammonium alkanesulfonate surfactants (alkane = methane, ethane, *n*-propane, *n*-butane) and proposed that lengthening the alkyl chains initially hinders micelle formation but that longer chains are

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Table 2. Influence of Counterion Hydrophobicity on the Cmc and Counterion Binding (β) of 1-Methyl-4-*n*-dodecylpyridinium Surfactants

surfactant	T (°C)	cmc (mM)	β (%)	$\sum f_i$[e]
4	30	6.9	53	0.702
	40	7.2	50	
	50	7.5	45	
	60	10.1	41	
5[a,d]	40	2.1	71	0.757
6[b,d]	40	2.6	60	1.232
7[c,d]	60	2.8	85	1.762
8	30	4.1	56	2.292

[a] $T_{krafft} = 37.1$ °C. [b] $T_{krafft} = 35.2$ °C. [c] $T_{krafft} = 53.0$ °C. [d] At the Krafft temperature the solubility of a given surfactant shows a sudden sharp increase.[8,20] Below these temperatures surfactants are only slightly soluble in water and the concentrations are below the cmc. [e] $\sum f_i$ is the sum of the hydrophobic fragmental constants of the hydrophobic part of the counterion.

markedly effective in lowering the cmc, owing to enhanced hydrophobic interactions between counterions and surfactant molecules in the micelles. The degrees of counterion binding[21] are 66% for methanesulfonate, 53% for ethanesulfonate, 61% for *n*-propanesulfonate, and 78% for *n*-butanesulfonate. The results were explained[21] in terms of different interaction modes between surfactant monomers and counterions at the micellar surface. The first two methylene groups attached to sulfonate ions cannot develop the usual hydrophobic hydration sphere as a consequence of strong sulfonate−water interactions.[22] This is in contrast with weak solute−water interactions (hydrophobic hydration) for the more remote methylene groups and the methyl group at the end of an alkyl chain.

Aromatic Counterions. Aromatic counterions have a marked influence on the aggregation of surfactants. They can penetrate in between pyridinium headgroups, thereby displaying specific counterion effects (e.g. interactions between the pyridinium ring, some of the methylene groups in the hydrophobic moiety, and the phenyl ring of the aromatic counterion). As a result they bind more strongly at the micellar surface[23] than bromide or chloride counterions, thereby reducing the cmc and increasing the degree of counterion binding. Apparently aromatic counterions interact with the micelles both electrostatically and hydrophobically. Furthermore, aromatic counterions can induce the formation of wormlike micelles. For example, cetyltrimethylammonium tosylate forms spherical micelles above 2.6 mM.[17] However, at still higher concentrations of surfactant, these aggregates start to grow beyond the cwmc (critical concentration for the formation of wormlike micelles), which is around 15 mM for this surfactant.[24] Salicylate is particularly effective with respect to micellar growth. In the case of cetyltrimethylammonium salicylate[25] no spherical micelles are formed at all, but instead long wormlike micelles are formed immediately at the cwmc.

These aggregates can become so long that they form entangled networks. The driving force behind this process will be discussed in a future paper.[26] We have systematically varied the substitution pattern in the aromatic ring of the counterion (**9**−**17**, Chart 1) and examined the impact of this variation on the aggregation of alkylpyridinium surfactants.

Degree of Penetration of the Aromatic Counterions into 1-Methyl-4-*n*-dodecylpyridinium Micelles. Quantitative information about the shape, size, and inner structure of micelles is of great relevance in surface and colloid chemistry. Various techniques have been widely used[27−31] in this field of research. We have applied ^{1}H-NMR to determine the position of aromatic counterions in alkylpyridinium micelles, using alkylpyridinium iodides as a reference. On the basis of the magnetic anisotropy effects of aromatic rings, information was obtained on the average location of the aromatic counterions at micellar binding sites.

Intercalation of aromatic counterions between headgroups of surfactants in micelles results in an upfield shift of some of the protons of the surfactant monomers in the aggregate as a result of a ring current-induced shift (Figure 1).

The binding process was monitored by a difference in chemical shift between ^{1}H-NMR signals for chemically identical hydrogen atoms of micelles formed by surfactants with aromatic and iodide counterions, respectively. The upfield (negative values in Figure 1) ^{1}H shifts are the largest for pyridinium protons (protons 3 and 4, Figure 1), indicating that the hydrophobic counterions are primarily located in this region of the Stern layer. The upfield shifts were observed for all aromatic counterions.

As shown in Figure 1, the most pronounced differences in surfactant proton chemical shifts are observed for surfactants with those counterions which produce viscoelastic solutions (compounds **15** and **17**). These upfield shifts indicate that the surfactant molecules in micelles formed by surfactants **15** and **17** are in a more apolar environment than those in micelles formed by surfactant **1** and that pyridinium headgroups and aromatic counterions are in rather close proximity. Presumably **15** and **17** are most effective in repelling water from micelles (i.e. the headgroup region) and allow counterions and headgroups to approach each other closely. The ^{1}H-NMR spectra of compounds **15** and **17** reveal a marked line broadening of the peaks from surfactant molecules (compared to the ^{1}H-NMR spectra of surfactant **1**), indicative of the presence of wormlike micelles. Some of the counterion peaks, however, are sharp and still show a splitting pattern. Apparently the surfactant monomers are strongly packed in the micelle and restricted in their movement, while the counterions retain more freedom to move. On the basis of ^{1}H-NMR spectra for cetyltrimethylammonium salicylate, Anet[32] concluded that salicylate ions have different tumbling motions in mobile nonviscoelastic solutions of cetyltrimethylammonium bromide/sodium salicylate and in viscoelastic micellar solutions. In viscoelastic solutions, salicylate ions tumble much faster about an axis parallel to the headgroup of the surfactant (C1−C4 axis of 2-hydroxybenzoate (salicylate) counterions) than about a perpendicular axis. This explains why some of the proton signals are relatively sharp.

Quite generally, spherical micelles grow upon increasing surfactant concentration and form wormlike micelles. The headgroups of surfactant monomers in wormlike micelles

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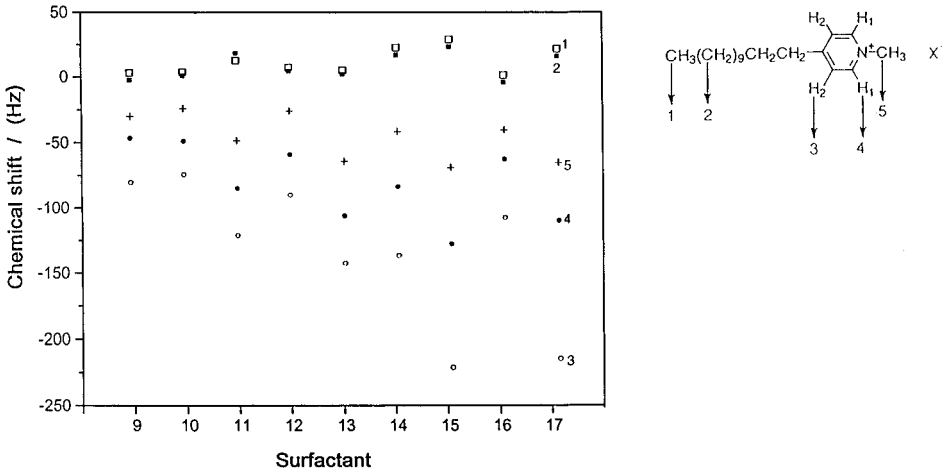

Figure 1. Chemical shifts relative to 1-methyl-4-*n*-dodecylpyridinium iodide, for 1-methyl-4-*n*-dodecylpyridinium surfactants with aromatic counterions (see Chart 1 for 'compound number'): □, protons 1; ■, protons 2; ○, protons 3; ●, protons 4; + protons 5. All measurements were performed in solutions in D_2O, at a concentration of twice the cmc.

are packed closer together than in spherical micelles. Therefore, the influence of the size of the 1-methyl-4-*n*-dodecylpyridinium iodide micelle was examined in relation with the proton chemical shifts. For 1-methyl-4-*n*-dodecylpyridinium iodide (**1**) the cmc is 2.5 mM, and the cwmc amounts to 45 mM.[7] ^{1}H-NMR spectra for this surfactant were recorded at concentrations of 20, 30, 50, and 90 mM, using a 5 mM solution in D_2O as reference. Effects similar to those recorded for surfactants having aromatic counterions were observed but were much smaller in magnitude. When the concentration of 1-methyl-4-*n*-dodecylpyridinium iodide was increased, the chemical shift differences were smaller by a factor between 4 and 10. For proton 3 (Figure 1), the upfield shifts were 6 Hz (20 mM), 9 Hz (30 mM), 12 Hz (50 mM), and 12 Hz (90 mM) relative to a 5 mM solution. For proton 4, the differences, relative to the 5 mM solution, were 15 Hz (20 mM), 18 Hz (30 mM), 21 Hz (50mM), and 24 Hz (90 mM). We contend that the observed upfield chemical shifts for 1-methyl-4-*n*-dodecylpyridinium surfactant with aromatic counterions primarily result from intercalation of aromatic counterions in between headgroups and are not due to differences in aggregation number.

Although the microenvironment may be different for the different aromatic counterions, the degree of counterion penetration is about the same for all surfactants studied. In all spectra of viscoelastic solutions the proton signal of water remains sharp, suggesting[33] that water molecules may be trapped in a gel-like structure but retain their mobility. It is concluded that the macroscopic viscosity of the solution is related to the entangled chains and is not due to an effect on the hydrogen bond network of water.

Influence of Aromatic Counterions on Cmc Values and Degrees of Counterion Binding for 1-Methyl-4-*n*-dodecylpyridinium Surfactants. Micelle formation is particularly facilitated if the aromatic counterion is readily dehydrated. Furthermore, the effect on micellar stability depends upon specific counterion effects, as dictated by the exact molecular architecture of the counterion. For surfactants **9** and **10** (Table 3), the cmc increases with decreasing hydrophobicity of the counterion and the degree of counterion binding decreases. For surfactants **12** and **13** we observe the same trend. Changing the position of the hydroxy group from para to meta to ortho positions has a large influence, which cannot

Table 3. Influence of Aromatic Counterions on the Cmc and Counterion Binding (β) of 1-Methyl-4-*n*-dodecylpyridinium Surfactants at 30 °C

surfactant	cmc (mM)	β (%)	Σf_i[b]
9	2.0	78	1.886
10	1.4	80	2.588
11	2.1	76	1.543
12	2.2	77	1.886
13	2.6	72	1.543
14	1.9	63	1.543
15	0.7[a]	87	1.543
16	3.4	69	2.115
17	0.7[a]	94	2.808

[a] Wormlike micelles are formed instead of spherical micelles. [b] Σf_i is the sum of the hydrophobic fragmental constants of the hydrophobic part of the counterion (the R moiety in the $R-COO^-$ or $R-SO_3^-$ counterion).

be explained solely on the basis of hydrophobicity. Surfactant **15** with the lowest cmc and the highest degree of counterion binding does not form spherical micelles but long wormlike micelles instead. The degree of counterion binding increases on going from spherical micelles to wormlike micelles.[34] Surfactant **17** also forms long wormlike micelles; the cmc is again low and the degree of counterion binding is relatively high, when compared to those of the counterions which promote aggregation into spherical micelles in dilute solutions above the first transition concentration. A difference in aggregation exists, however, between surfactants **15** and **17**. It is often assumed that salicylate and *p*-chlorobenzoate have the same influence on surfactant aggregation,[35] because both are thought to give rise to a network of entangled wormlike micelles above the cwmc. However, a significant difference exists. Aqueous solutions of surfactant **15** are viscoelastic above 0.7 mM (C > cwmc), but aqueous solutions of surfactant **17** are not viscoelastic in the region 0.7−1.2 mM. At concentrations above 1.2 mM (cwmc = 0.7 mM), the initially formed aggregates entangle. *o*-methoxybenzoate (surfactant **16**) is far less effective in facilitating micellization. Compared to the case of surfactant **12,** the cmc increases and the degree of counterion binding decreases. It appears that introduction of an *o*-methoxy group increases headgroup repulsions and hampers micellization. Presumably, the *o*-methoxy group fits less well between the headgroups in the Stern region. Surfactant **16** forms spherical micelles above 3.4 mM, whereas

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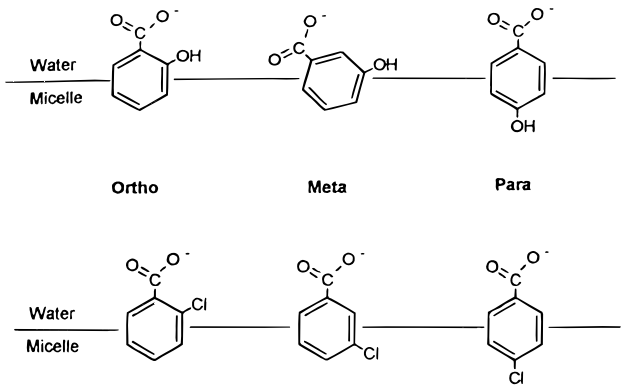

Figure 2. Orientations of *x*-hydroxy- or *x*-chloro-substituted benzoate counterions at the micelle−water interface, as deduced from NMR measurements.[36]

surfactant **15** forms an entangled network of long wormlike micelles already at concentrations just above 0.7 mM. This difference points to the importance of hydrogen bonding involving the counterion at the micellar surface in stabilizing micelles and in facilitating micellar growth.

Changing the position of the hydroxy group from para (**13**) to meta (**14**) to ortho (**15**) in 1-methyl-4-*n*-dodecylpyridinium *x*-hydroxybenzoate surfactants lowers the cmc (or the cwmc in the case of **15**). This pattern can be explained by taking the microenvironment of the counterions into account[36] (Figure 2). A hydroxy group at the para position leads to a relatively unfavorable enviroment for this substituent. Therefore, compared to the case of **15**, the higher cmc and lower degree of counterion binding for **13** are anticipated. Meta substitution leads to a more favorable environment (the hydroxy group now points into the Stern region), but the counterion is "tilted". A "tilted" orientation was also proposed by Iyer et al.,[33] who studied the ^{1}H-NMR spectra of salicylate and 3-hydroxybenzoate bound to cetyltrimethylammonium micelles. The most favorable situation, however, is found for the salicylate counterion, as evidenced by the low cwmc and high counterion binding.

Interestingly, surfactant **17** also forms wormlike micelles at a low cwmc and has a high degree of counterion binding. Upon micellization the relatively hydrophobic *p*-chloro substituent is placed in an environment comprising only headgroups and penetrated water. This favorable position compared to that of the *o*-chlorobenzoate surfactant might explain the aggregation behavior of surfactant **17**, consistent with the reasoning developed above for the salicylate counterions.

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Conclusion

Subtle changes in counterion structure are shown to have a large influence on the aggregation behavior of alkylpyridinium surfactants. It has been shown that the critical micelle concentration increases when the hydrated size of the counterion increases, whereas the degree of counterion binding decreases. For alkanesulfonate counterions, the hydrophobicity of the counterion should also be taken into account. More hydrophobic counterions usually result in lower critical micelle concentrations and higher degrees of counterion binding. For aromatic counterions, these arguments remain valid; however, also the substitution pattern in the aromatic ring and the microenvironment at the binding site exert a specific effect. Ortho-hydroxy substituents illustrate this situation the best, counterion−water interactions become even dominant, and the 1-methyl-4-*n*-dodecylpyridinium surfactants aggregate into extremely long wormlike micelles instead of spherical micelles. When the hydroxy group is placed in a less favorable microenvironment due to its positioning (e.g. meta or para), the aggregation behavior is drastically altered due to a less favorable solvation at the micellar surface. NMR line shift experiments revealed that all aromatic counterions penetrate in between surfactant headgroups of the micellar aggregate. It is concluded that the differences in aggregation behavior of 1-methyl-4-*n*-dodecylpyridinium surfactants with aromatic counterions are indeed due to differences in the various interaction modes and not due to differences in the degrees of penetration of counterions in between pyridinium headgroups.

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